Safe and Efficient Disposal of Hexachlorodisilane Liquid

Thanh-Trung Nguyen[a], Yu-Wen Huang[a], Pei-Xuan Yan[a], Yu-Chun Hu[a],
Hsiao-Yun Tsai [a] , Jenq-Renn Chen [a,*] , Eugene Y. Ngai[b]

[a] Department of Safety, Health and Environmental Engineering, National Kaohsiung University of Science and Technology,
  Kaohsiung, Taiwan
[b] Chemically Speaking LLC, Whitehouse Station, New Jersey 08889, United States.
  jrc@nkust.edu.tw

This research project was to develop a safe and efficient method for disposal of HCDS liquid in large quantities. The proposed method is a two-stage process which includes direct hydrolysis of HCDS liquid in water, followed by alkaline cleavage of the hydrolyzed product in aqueous suspension by an aqueous potassium hydroxide (KOH) solution. In the first stage, HCDS liquid was directly hydrolyzed in water. The required ratio of HCDS to water was 1:25 by weight. During the hydrolysis, the reaction was mild and took place without significant fuming. There was a new peak at 915 cm^{-1} observed only in the IR spectrum of the liquid HCDS hydrolyzed deposit hydrolyzed in water that may be attributed to the existence of small silicon-oxide molecules in the cluster. It was determined that, unlike other hydrolyzed deposits formed in moist air, the liquid HCDS hydrolyzed deposit formed in water was readily reactive to alkaline solution at ambient conditions with a concurrent release of hydrogen gas. In the second stage, aqueous KOH solution (20 wt%) was then added to neutralize the suspended solution. The required weight ratio of KOH to HCDS was 2:1 to get a final pH of about 12.6. The residual deposit was completely dissolved in two hours.
Keywords: Hexachlorodisilane, HCDS, hydrolyzed deposit, shock sensitive, disposal.

1. Introduction

Hexachlorodisilane (Si_2Cl_6, HCDS) is an emerging and important silicon-containing precursor in semiconductor manufacturing and related industries. HCDS is readily hydrolyzed by moisture or water to form silicon oxides and corrosive hydrogen chloride. The hydrolyzed deposit of HCDS as well as other polychlorosilanes has been proven to be sensitive to mechanical impact. It caused a fatal explosion at a high-purity polycrystalline silicon manufacturing facility in Japan in 2014 resulting in 5 fatalities and 13 injuries (Mitsubishi Materials Corporation, 2014).

In the past few years, Lin and her partners developed several methods for safe disposal of HCDS vapor and its hydrolyzed deposits (Lin et al., 2019; Lin et al., 2020). Based on the fact that Si-Si bonds in chlorosilanes can be broken up when the hydrolysis takes place in an alkaline solution, they were proven to be effective with HCDS by an alkaline cleavage reaction. Although aqueous KOH solution was found to be an effective abatement solution for HCDS, the byproducts quickly caused clogging in the HCDS feed tube due to prompt hydrolysis.

Alcoholic alkaline solutions have been determined to be effective in decomposing HCDS vapor without the clogging problem. However, disposal of HCDS vapor requires a lot of time since the disposal rate was 0.1 g/min (Lin et al., 2020). Additionally, there remains a risk of fire from flammable alcoholic alkaline solution.

The safe disposal of HCDS liquid, important for handling HCDS liquid spill, is extremely difficult due to the potential for violent and explosive reactions of direct alkaline attack. The main purpose of this research is to develop a safe and efficient method to dispose HCDS liquid on a large scale.

2. Materials and methods

2.1 Materials

Semiconductor grade HCDS was supplied by Air Liquid Advanced Materials, USA, with a purity of 99.5% by gas chromatography. Potassium hydroxide (KOH) pellets were obtained from Nihon Shiyaku, Japan, with assay of 85%, a maximum of 1.5% potassium carbonate (K_2CO_3), and the remainder being water.

2.2. Proposed disposal method for HCDS liquid

The proposed method is a two-stage process direct hydrolysis of HCDS liquid in water, followed by addition of alkaline solution into the resulting suspension as shown in Figure 1.

Stage 1. Hydrolysis HCDS liquid in bulk water

The experiments were carried out in a nitrogen glovebox to prevent fire and explosion due to H_2 evolution during the HCDS disposal. To avoid clogging at the feed nozzle, liquid HCDS was fed into the vapor space of the water bath. The HCDS flow rate of approximately 20 g/min was controlled directly using a needle valve. To minimize the evolution of gaseous HCl, excess water with a ratio of HCDS to water of 1:25 by weight was used; a mechanical stirrer equipped with a propeller was used to mix the reactants throughout the experiment with a speed of 1000 revolution per minute (rpm). The resulting suspension in the first stage contained white hydrolyzed deposit and HCl. It is very important to note that this proposed HCDS abatement method is only effective when HCDS hydrolyzes in liquid water. As soon as HCDS contacts water, the hydrolysis reaction occurs immediately on the surface of the water and tends to form a passive oxide film on the HCDS liquid surface that prevents the hydrolysis from taking place completely. Therefore, stirring must be used to intimately mix the HCDS liquid with the water. HCDS hydrolyzed by vapor water on the surface instead of by bulk water yields a different hydrolyzed deposit structure. A tracking method in which plastic beads lighter than water or dye was used to evaluate the mixing efficiency before performing the HCDS hydrolysis. Additionally, avoiding hydrolysis on the surface of water will favor the absorption of gaseous HCl in water.

Stage 2. Neutralization the hydrolysis products

In the second stage, aqueous KOH solution (20 wt%) was subsequently fed into the resulting suspension. The required weight ratio of KOH to HCDS was 2:1 to get a final pH of approximately 12.6. pH and temperature were monitored throughout the experiment. For safety reasons, the H_2 concentration was diluted to less than 4 vol.% by adjusting the N_2 purge flow rate.
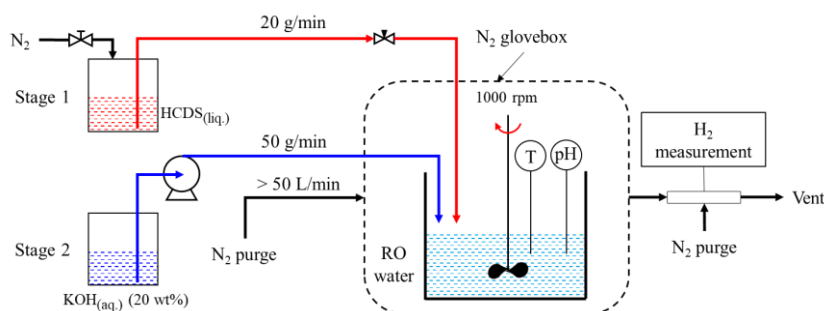

Figure 1: Schematic diagram for disposal of HCDS liquid

3. Results and Discussion

3.1 Direct hydrolysis of HCDS liquid in liquid water

The formation of HCDS hydrolyzed deposits and the remaining Si-Si bonds in the deposit are summarized in Table 1. The ratio of consumed HCDS to produced dried hydrolyzed deposit was 1:0.42 by weight. The amount of Si-Si bonds in the deposit was deduced from the volume of H_2 generated during the reaction with aqueous KOH solution. More than 84% of the initial Si-Si bonds was preserved during hydrolysis of HCDS in bulk water which basically agrees with the 90% reported by Belot et al. (1991).

Table 1: Hydrolysis of HCDS in liquid water

Test #	Used HCDS (g)	Dried obtained deposit (g)	Deposit/ HCDS (g/g)	Theoretical Si-Si bond quantity in deposit (bond/g)[a]	H_2 released from deposit (mL/g)	Actual amount of Si-Si bond in deposit (bond/g)[b]	Remaining Si-Si bonds (%)
1	66.87	27.52	0.41	5.440×10^{21}	188.1	4.586×10^{21}	84.3
2	79.68	33.42	0.42	5.349×10^{21}	188.2	4.588×10^{21}	85.8

[a] the number of Si-Si bonds with an assumption that no Si-Si cleavage occurred during hydrolysis
[b] the number of Si-Si bonds in the deposit calculated based on volume of H_2 release in the complete reaction with aqueous KOH solution at 29 °C

The hydrolyzed deposit was sent for FTIR analysis right after complete hydrolysis without further drying. Figure 2 compares the IR spectrum of liquid phase HCDS hydrolyzed deposit in water with different hydrolyzed deposits formed in moist air. The bands at 3250 and 1630 cm^{-1} are attributed to OH-stretching and bending regions of

water, respectively (Wang et al., 2004). The band at 3250 cm^{-1} also can be assigned to the hydrogen-bonded silanol groups (Smith et al., 1991). The 1000 cm^{-1} band is attributed to the asymmetric stretching mode of the Si-O-Si structure arising from the condensation of two silanol groups (Belot et al., 1991). The band at 870 cm^{-1} can be used as an indication of the Si-Si bonds in the structure of HCDS hydrolyzed deposits (Lin et al., 2019; Lin et al., 2020). A weak band at 725 cm^{-1} can be assigned to Si-O-Si bending vibration (Ahsan & Mortuza, 2005). It was a surprise to find that there is a new peak at 915 cm^{-1} observed only in the IR spectrum of the liquid HCDS hydrolyzed deposit hydrolyzed in water that may be attributed to the existence of small silicon-oxide molecules in the cluster (Chmel et al., 1990). It is important to note that the reaction of aqueous KOH solution and HCDS hydrolyzed deposit was found to be highly dependent on the deposit size as reported by Nguyen et al. (2021). The new finding on such smaller silicon oxide molecule is the main key in the large-scale HCDS disposal method in which the dissolution of hydrolyzed deposit in aqueous alkaline solution is expected to be faster than that of a deposit hydrolyzed in moist air.
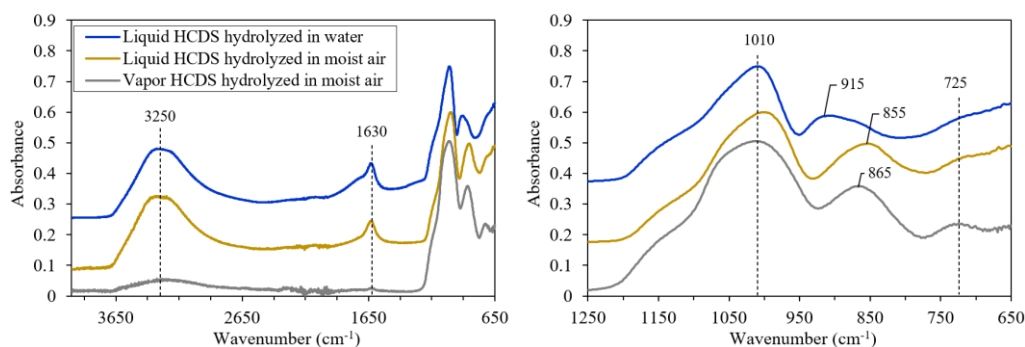

Figure 2: Comparison of FTIR spectra of various HCDS hydrolyzed deposits

The intensity of 915 cm^{-1} band slightly decreases after 60 minutes of drying by vacuum with significant removal of water; after 90 minutes drying at 105 °C, the band 915 cm^{-1} disappears. According to Chmel et al. (1990), the disappearance of 915 cm^{-1} band implies the formation larger silicon oxide molecules due to polymerization. More important, the band 915 cm^{-1} did not appear again when rewetting the dried deposit for more than 7 hours. During the drying process, the bands at 1010 and 725 cm^{-1}, which are attributed to Si-O-Si asymmetric stretching and bending also shifted to 1025 and 750 cm^{-1}, respectively. The shifts of those bands are attributable to the oxidation of Si-Si bonds in the hydrolyzed deposit (Nguyen et al., 2021). It is noted that those shifts did not occur with other deposits hydrolyzed in moist air when drying at 105 °C, indicating that the part of Si-Si bonds in the deposit hydrolyzed in water are more readily to be cleaved by heat treatment in the aqueous solution.
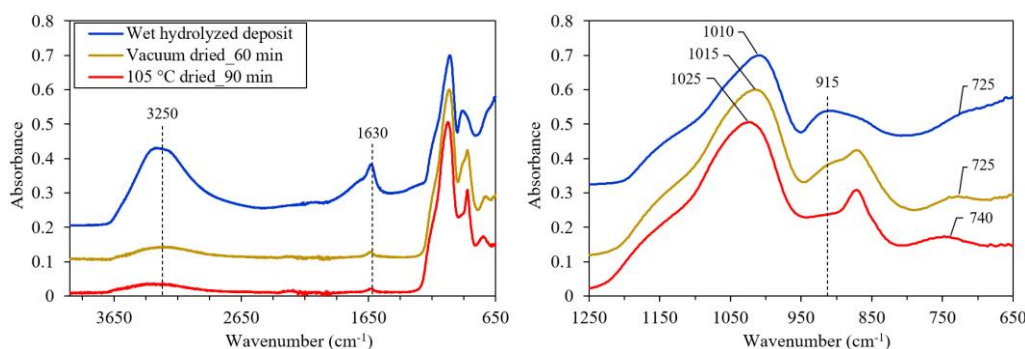

Figure 3: IR band 915 cm^{-1} during drying process

3.2 Reactivity of hydrolyzed deposit in water and KOH solution

The reactivity testing of hydrolyzed deposits in water and aqueous KOH solution was done by adding approximately 0.5 g of hydrolyzed deposit into 250 mL of test solution. The H$_2$ evolution, used as indication of reaction, was measure by a eudiometer during reaction of the deposit with water (Figure 4a) and 20 wt% aqueous KOH solution (Figure 4b). Clearly, the deposit reacts with both solutions. For the reaction with water, H$_2$ emitted in the first 30 hours of reaction with approximately 129 ml/g of deposit that was equivalent to 69% of Si-Si bonds broken. The reaction of the deposit and KOH solution was found to be significantly faster than in water, no further H$_2$ was released after 3.5 hours of reaction with 188 mL/g of H$_2$ generated, corresponding to 100% of Si-Si bonds broken (Table 1) and the solution turned completely transparent.

Figure 5 compares the IR spectra of hydrolyzed deposits before and after emerging in water (pH of 6.5) for more than 60 hours. The bands at 1010 and 725 cm^{-1} assigned to Si-O-Si asymmetric stretching and bending shift to higher wavenumber of 1060 and 800 cm^{-1}, respectively. Furthermore, the band at 870 cm^{-1}, indication of the presence of Si-Si bonds, was found to be almost diminished. Clearly, the Si-Si linkages in hydrolyzed deposit was dramatically oxidized in water to SiO$_2$, which is indicated by the presence of 800 cm^{-1} band attributed to Si-O bending vibrational mode of SiO$_2$ (Moore et al., 2003). More importantly, the dried residual deposit was found to be non-flammable to torch and non-impact sensitive at the energy of 50 J.
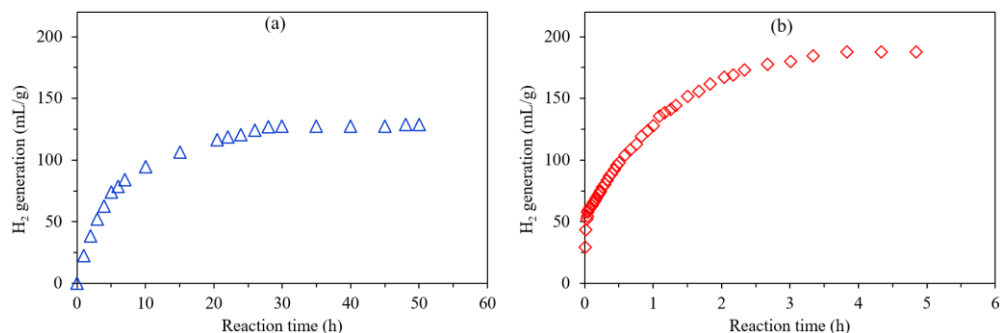

Figure 4: H$_2$ evolution during the reaction of hydrolyzed deposit with (a) RO water and (b) 20 wt% aqueous KOH solution at 29 °C
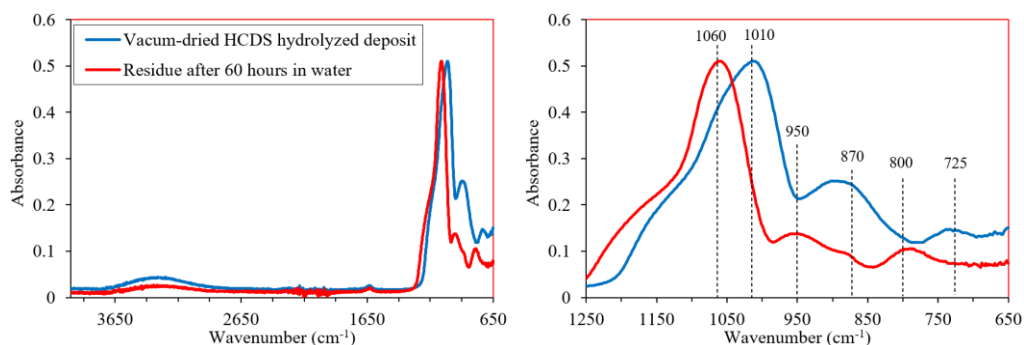

Figure 5: FTIR comparison of hydrolyzed deposit before and after reaction in RO water for 60 hours

3.3 Calorimetric investigation

Before scaling up the new HCDS disposal method, a calorimetric investigation of HCDS disposal in aqueous alkaline solution was carried out in which heat involved in each stage was measured by reaction calorimeter (RC) power compensation principles. The reactions including hydrolysis of HCDS liquid in water, oxidation of HCDS hydrolyzed deposit in aqueous KOH solution, and HCDS in aqueous KOH solution was determined at 30 °C. The heat release of each reaction was converted to be per unit mass of HCDS.

To determine the heat from the cleavage of Si-Si in HCDS, the hydrolyzed deposit was washed to remove residual HCl before calorimetric analysis. The washed deposit was mixed well and divided into two parts, one for RC analysis and the rest for H$_2$ evolution analysis. The heat released from the reaction of the deposit and KOH aqueous solution was determined to be 2279.8 J/g (deposit) with the total H$_2$ evolved of 171.6 ml/g (deposit). The relationship between heat release and H$_2$ evolution at 29 °C can be described as:

$$\frac{2279.8 \frac{J}{g_{(deposit)}}}{171.6 \frac{mL_{(H_2)}}{g_{(deposit)}}} = \frac{2279.8 \text{ J}}{171.6 \text{ mL}_{(H_2)} \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{1 \text{ mol}}{24.7 \text{ L}}} = \frac{2279.8 \text{ J}}{6.95 \times 10^{-3} \text{mol}_{(H_2)}}$$

In general, the cleavage of 1 Si-Si bond yields 1 molecule of gaseous H$_2$; therefore, disposal of 1 molecule of HCDS, which contains 1 Si-Si bond will release 1 molecule of H$_2$. Hence, the heat release from the cleavage of Si-Si bond in HCDS can be estimated as:

$$\frac{2279.8 \text{ J}}{6.95 \times 10^{-3} \text{mol}_{(HCDS)}} = \frac{2279.8 \text{ J}}{6.95 \times 10^{-3} \text{mol}_{(HCDS)} \times 269 \frac{g_{(HCDS)}}{mol_{(HCDS)}}} = 1219.9 \frac{J}{g_{(HCDS)}}$$

The heat of neutralization was calculated based on the heat released from the reaction of HCl and KOH:

$$\text{KOH} + \text{HCl} \rightarrow \text{KCl} + \text{H}_2\text{O} \left(\Delta H = -57.2 \frac{kJ}{mol} \right)$$
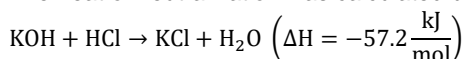
The complete hydrolysis of 1 mole of HCDS yields 6 moles of HCl. Therefore, the heat release from the neutralization reaction can be calculated as:

$$6 \times 57.2 \frac{kJ}{mol_{(HCDS)}} = \frac{57.2 \times 6 \frac{kJ}{mol_{(HCDS)}}}{269 \frac{g_{(HCDS)}}{mol_{(HCDS)}}} = 1.276 \frac{kJ}{g_{(HCDS)}} = 1276 \frac{J}{g_{(HCDS)}}$$

Based on the estimated total heat release from the HCDS disposal process as summarized in Table 2, adequate water can be used to control the reaction temperature and avoid a violent reaction.

Table 2: Heat release from HCDS disposal process

Reactions	Heat release
Hydrolysis of HCDS liquid in water (Stage 1)	1455.8 J/g of HCDS
Cleavage of Si-Si bond (Stage 2)	2279.8 J/g of deposit
	1219.9 J/g of HCDS
Neutralization reaction (Stage 2)	1276.0 J/g of HCDS
Total	3951.7 J/g of HCDS

3.4 Abatement of hydrolysis products

The abatement stage was carried out right after the hydrolysis of 200 g of HCDS liquid in water. In this stage, 20 wt.% aqueous KOH solution was used to neutralize the resulting solution and break Si-Si bonds in the hydrolyzed deposit. The rate of H_2 release and pH during the abatement of hydrolysis products are shown in Figure 6. Initially, KOH was fed into the solution with high-dose rate of 10 to 20 g/min. In the pH range less than 5, no H_2 was detected. H_2 started releasing when the solution reached pH 5 at which the dose rate of KOH was adjusted to 0.5 g/min to slow the reaction. The majority of the H_2 generated was in the pH range of 5 to 7 with a peak release rate of approximately 870 ml/min. The H_2 release rate dropped approximately 200 ml/min to when the solution reached pH 7, KOH was then added with high-dose rate to quickly get to a pH of 12.6 in order to enhance dissolution of oxide deposit that generally takes place quickly in alkaline solution. When reaching pH 12.6, the resulting solution was allowed to react until the reaction was complete. It can be seen from Figure 7 that the solution turned completely transparent after 2 hours of reaction.
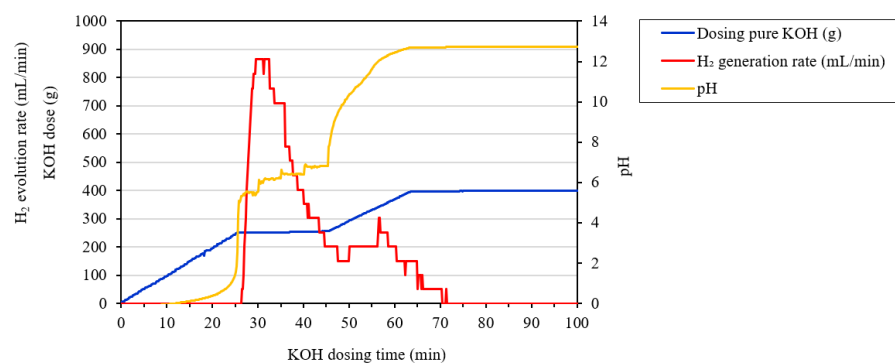

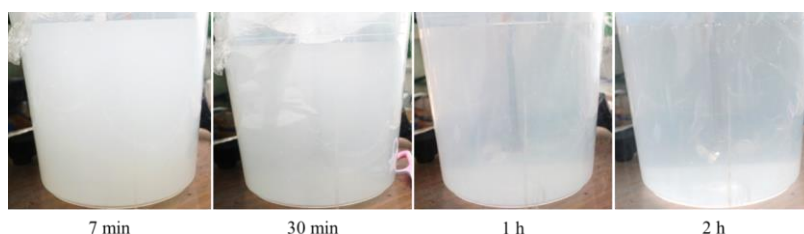*Figure 6: H2 evolution during abatement stage*

Figure 7: Dissolution of hydrolyzed deposit in alkaline solution (pH 12.6)

Table 3 summarizes the results of liquid HCDS disposal tests. The reaction was found to be mild for each stage. The temperature rises during HCDS liquid hydrolysis in liquid water were consistent with those estimated from the calorimetric investigation as summarized in Table 2. The temperature rises during KOH addition were found to be lower than the estimated one most likely owning to the heat dissipation from the solution to ambient

environment during the long period of KOH dosing. Clearly, the proposed method is safe and efficient to dispose of HCDS in a large scale as the process could be done within four hours. The final solution contains non-flammable/non-toxic products including potassium silicate, KCl and KOH.

Table 3: The results of liquid HCDS disposal

Test #	HCDS weight (g)	HCDS Feeding rate (g/min)	Water weight (g)	KOH weight (g)	KOH dosing rate (g/min)	Hydrolysis (stage 1)		KOH addition (stage 2)	
						Est. ΔT (°C)	Exp. ΔT (°C)	Est. ΔT (°C)	Exp. ΔT (°C)
1*	50	14.3	500	97.8	5.5	34.8	35.5	24.8	7.7
2	100	20.0	2500	192.2	8.93	13.9	13.6	17.1	13.3
3	200	19.4	5000	392.4	8.77	13.9	14.1	17.1	11.4
4	200	-	5000	400.0	1.01	13.9	-	17.1	12.9
5	200	12.1	5000	393.6	5.6	13.9	13.8	17.1	11.4

*14 wt% aqueous KOH solution was used in the stage 2

4. Conclusions

In conclusion, the proposed two-stage disposal method for HCDS liquid has been demonstrated to be safe and effective. In the first stage, HCDS liquid was directly hydrolyzed in liquid water with sufficient stirring. Heat release from this stage was determined to be 1455.8 J/g of HCDS. The hydrolyzed deposit was found to be readily reactive to aqueous KOH solution. In the second stage, 20 wt.% aqueous KOH solution was used to neutralize the resulting solution. H_2 gas was detected as soon as the solution reached pH 5. KOH dosing rate could be adjusted to control the H_2 generation rate. The total heat release in the second stage was determined to be 2495.9 J/g of HCDS. After 2 hours at pH 12.6, the solution turned transparent, indicating that the dissolution of HCDS hydrolyzed deposit was complete. It is very important to note that continuous H_2 monitoring and dilution are required to prevent the released H_2 from igniting.

References

Ahsan, M. R., & Mortuza, M. G., 2005, Infrared spectra of xCaO(1−x−z) SiO2zP2O5 glasses, Journal of Non-Crystalline Solids, 351(27-29), 2333-2340.

Belot, V., Corriu, R., Leclercq, D., Lefevre, P., Mutin, P., Vioux, A., & Flank, A., 1991, Sol-gel route to silicon suboxides. Preparation and characterization of silicon sesquioxide, Journal of Non-Crystalline Solids, 127(2), 207-214.

Chmel, A., Mazurina, E., & Shashkin, V., 1990, Vibrational spectra and deffect structure of silica prepared by non-organic sol-gel process, Journal of Non-Crystalline Solids, 122(3), 285-290.

Lin, Y.-J., Liu, C.-H., Chin, M.-G., Wang, C.-C., Wang, S.-H., Tsai, H.-Y., Chen, J.-R., Ngai, E. Y., & Ramachandran, R., 2019, Characterization of Shock-Sensitive Deposits from the Hydrolysis of Hexachlorodisilane, ACS Omega, 4(1), 1416-1424.

Lin, Y.-J., Nguyen, T.-T., Chin, M.-G., Wang, C.-C., Liu, C.-H., Tsai, H.-Y., Chen, J.-R., Ngai, E. Y., & Ramachandran, R., 2020, Disposal of hexachlorodisilane and its hydrolyzed deposits, Journal of Loss Prevention in the process industries, 104136.

Mitsubishi Materials Corporation, 2014, Investigative Report by the Accident Investigation Committee for the Explosion & Fire Accident occurred in the High-Purity Polycrystalline Silicon Manufacturing Facility at Yokkaichi Plant of Mitsubishi Materials Corporation. http://www.mmc.co.jp/corporate/en/news/2014/pdf/news20140612_2.pdf.

Moore, C., Perova, T. S., Kennedy, B. J., Berwick, K., Shaganov, I. I., & Moore, R. A., 2003, August 27, Study of structure and quality of different silicon oxides using FTIR and Raman microscopy, Opto-Ireland 2002: Optics and Photonics Technologies and Applications.

Nguyen, T.-T., Lin, Y.-J., Lin, Z.-X., Tai, H.-C., Tsai, H.-Y., Chen, J.-R., & Ngai, E. Y., 2021, Enhanced friction and shock sensitivities of hexachlorodisilane hydrolyzed deposit mixed with KOH, Journal of Loss Prevention in the process industries, 104455.

Smith, A. L., Winefordner, J. D., & Kolthoff, I., 1991, The analytical chemistry of silicones (Vol. 112), Wiley-Interscience.

Wang, Z., Pakoulev, A., Pang, Y., & Dlott, D. D., 2004, Vibrational substructure in the OH stretching transition of water and HOD, The Journal of Physical Chemistry A, 108(42), 9054-9063.